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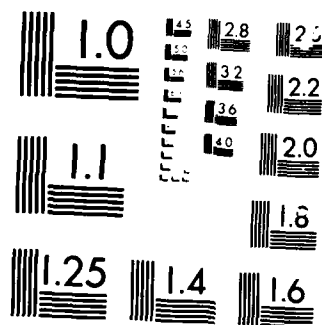
REACTIONS OF LASER-GENERATED FREE RADICALS AT
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Reactions of laser-generated free radicals at semiconductor surfaces have been investigated by photoelectron spectroscopy of adsorbed surface layers and by laser-induced fluorescence detection of the gas-phase species. Systems investigated include dissociative chemisorption of XeF_2 and CF_3 on $\text{Si}(111)$, IR multiple-photon dissociation of alkylsilanes and characterization of SiH_2 . Theoretical calculations of spectroscopic, structural, and thermodynamic properties of reactive free-radical intermediates have also been undertaken.

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FINAL REPORT

to the

AIR FORCE OFFICE OF SCIENTIFIC RESEARCH

on

Grant No. AFOSR-83-0007

"Reactions of Laser-Generated Free Radicals
at Semiconductor Surfaces"

by

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(25 November 1985)

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There is considerable interest in gaining an understanding of the chemical mechanisms involving reactive gas-phase species at semiconductor surfaces. These reactions may lead to either etching (transport of material from the surface as volatile products) or deposition of thin films on the surface. Both of these processes are essential steps in the fabrication of microelectronic devices.

The current state-of-the-art in etching and deposition is the RF plasma technique. While this technique is effective, its fundamental mechanisms are still poorly understood, which makes it difficult to extend the technique beyond its present limits, e.g., to submicron definition (VLSI) or to new materials. We have been carrying out an interrelated series of investigations addressing these problems, viz.: (1) detailed analysis of surface-adsorbed species and desorbed products in etching reactions of semiconductors, principally silicon; (2) optical probes for reactive gas-phase species; (3) improved understanding of plasma processes; and (4) generation of surface-active species by infrared multiple-photon dissociation (IRMPD).

An ultra-high vacuum apparatus for surface analysis measurements, incorporating a quadrupole mass spectrometer, UPS, XPS, LEED, Auger, and optical access for infrared radiation has been completed. Initial experiments have been directed toward characterizing the interaction of free fluorine with single-crystal Si(111)7x7, using XeF₂ as the fluorine source. A product with (m/e) = 85, attributed to either SiF₃ or SiF₄, desorbes in the neighborhood of 250°C, while SiF₂ begins to appear as the more fluorinated product tails off and peaks at ~400°C. At higher XeF₂ doses, the yield of SiF₃ (SiF₄) increases dramatically, but that of SiF₂ is essentially constant. These results suggest the presence of at least two distinct sites on this surface, one leading to SiF₄ formation and the other producing SiF₂. X-ray photoelectron spectroscopy

of the F(1s) level have shown that only one type of fluorine is observed on a stable overlayer in this system. At very high dosage levels, additional features appear in the F(1s) and Si(2p) XPS line, and SiF₄ [*m/e* = 104] is observed as a desorption product. These and related results can be explained by migration of F atoms in the lattice, either vertically from bulk to surface sites or laterally from one binding site to another.

Experiments are currently under way using fluorocarbon etchants (C₂F₆, CF₃I). A very slow spontaneous decomposition occurs with CF₃I ($\alpha_r \approx 10^{-7}$), producing adsorbed CF₂ and CF₃ moieties and leading to desorption of SiF₂ and SiF₃ products. Dissociation of the C₂F₆ by IRMPD results in chemisorbed C and F on the surface; from the XPS peak positions, it appears that most of the F atoms are transferred from C to Si in the adsorption process. The presence of coadsorbed adventitious hydrocarbons blocks the F atom transfer process. (Joyce *et al.*, 1984; Roop *et al.*, 1985).

An apparatus has been completed in which reactive species (CF₂, SiF₂, SiH₂, CF₃, etc.) may be produced by either infrared multiple-photon dissociation or u.v. photolysis, or generated in a d.c. discharge. Laser-induced fluorescence is used for quantitative detection of these species in the gas phase and following interaction with surfaces. Initial measurements using this technique have concentrated on the reactions of CF₂, detected via its $\tilde{A}-\tilde{X}$ transition at 261 nm, with Si and SiO₂. A simple reaction-diffusion model predicts the radical concentration *n*(*z*) to depend on vertical distance from the surface, *z*, in a simple linear fashion, from which the net surface reaction probability α_r can be determined. The data for CF₂ yield values of $\alpha_r = (0.021 \pm 0.007)$ for Si(111), $\alpha_r = (3.5 \pm 0.4) \times 10^{-3}$ for SiO₂.

SiH₂ has been detected (via its $\tilde{A}^1B_1 - \tilde{X}^1A_1$ transition) following IRMPD of organosilanes. The radiative lifetimes of rovibronic levels of the \tilde{A} state

show a wide variation, which is attributed to mixing with the \tilde{a}^3B_1 state (Thoman and Steinfeld). Analysis of these perturbations is presently under way.

Several theoretical investigations related to the experimental program have also been carried out. An analytical model has been developed for the electric potentials of a plasma and both electrodes in a diode type RF discharge. This model gives better agreement with experiment than the previous model of Koenig, and reproduces the numerical calculations of Keller and Pennebaker (Suzuki et al.). Also, since the spectroscopic properties of many of the reactive species of interest are not well known, ab initio calculations of these properties have been undertaken. Structural, spectroscopic, and thermochemical properties have been calculated at the 3-21G/SCF level for trifluoromethoxy, -methyltrioxy, and related free-radical species (Francisco et al., 1985; Francisco, 1985; Francisco and Williams, 1985).

Our principal technique for generating these free radicals is infrared multiple-photon dissociation (IRMPD). Since our understanding of the IRMPD process is far from complete, we have undertaken a number of studies designed to elucidate the details of this process. These have included master-equation modelling of IRMPD in chloroethane (Francisco et al., 1983) and the use of laser-induced fluorescence to probe vibrational levels of thiophosgene in a molecular beam following CO₂ laser excitation (Brenner et al., 1983). More recently, we have been using CARS to probe CO₂-laser-excited molecules, including chloroethane. A retrospective of our work on infrared laser photochemistry has been prepared for publication in an edited series (Francisco and Steinfeld, in press).

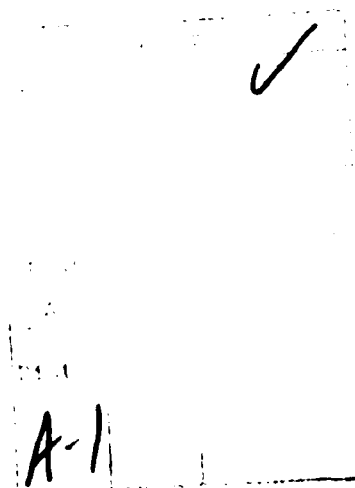
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